Lithene™ Liquid Polybutadienes, Versatile Rubber Modifiers

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Hydrophobicity **Flexibility** **Electrical insulation** **Chemical resistance** **Oil & Solvent compatibility** **Adhesion**

Lithene™ liquid polybutadiene summary properties

- 100% Active, plasticising liquid butadiene rubbers
- Very low Tg to –93°C
- Non hazardous
- Range of molecular weights and structures

Lithene™ liquid polybutadienes are unsaturated, low molecular weight polymers which can bring processing, performance and environmental benefits to a variety of rubbers and elastomers. Liquid polybutadienes (LPBd's) are part of a family of liquid rubbers which includes isoprene, styrene butadiene and various functionalised derivatives. Each type brings its own specific benefits to rubber compounds offering the formulator a choice of approaches to achieve the required product specifications.

This article will focus on two types of liquid rubber; pure liquid polybutadiene and polybutadiene functionalised with maleic anhydride. While these industrial polymers are widely used in many applications from electrically insulating resins to urethane modifiers and mold release additives, they also offer the rubber formulator benefits which will be demonstrated in the following examples.

Manufacture

LPBd's are derived from 1,3 butadiene, a highly reactive C4 monomer. Several recognised chemistry routes are open for polymerization of butadiene offering the potential to make polymers of diverse molecular weights and structures. LPBd's are typically characterised by their molecular weight and the relative content of C=C unsaturation in different arrangements. While some LPBd's have a very high degree of in-chain 1,4 double bonds in cis or trans configurations, Figure 1 represents structures typically found in Lithene polymers, which combine 1,4, 1,2 vinyl and 1,2 cyclic vinyl arrangements. These structural differences impact the viscosity of the liquid polymer but more importantly affect reactivity in different cure chemistries and the nature of subsequent bonding and network formation.

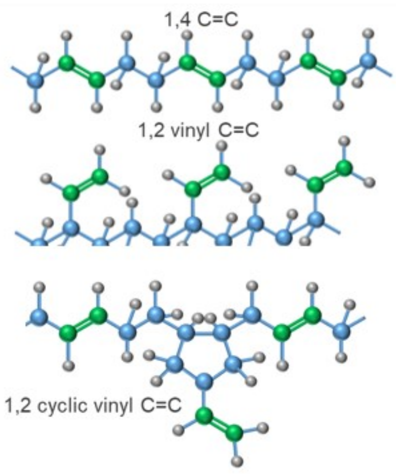


Figure 1. C=C Structure combinations Lithene

Table 1. Lithene grades and key properties

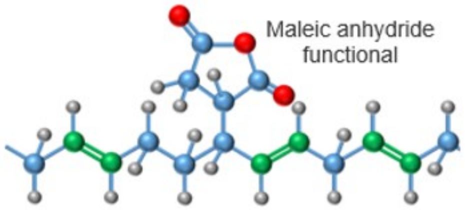
LPBd	Mwt. Mn Da	PDi	1,2 Vinyl %	Tg °C
Lithene *ultra* N4-5000	5000	Narrow	15	-93
Lithene*ActiV* 1000	2800	Broad	75	-39
Lithene *ultra* PH	2600	Broad	45	-70

Table 1. demonstrates how the combined effect of polymer molecular weight and C=C type, have a significant influence on product viscosity. Steric effects particularly associated with the 1,2 vinyl and cyclic structures contribute strongly to viscosity build, but can be reduced significantly by heating the polymer during processing.

Functional Lithene Grades

Once the base polybutadiene chain has been produced, maleic anhydride can be grafted to form a succinic anhydride adduct as represented in Figure 2.

Figure 2. Maleic anhydride grafted Lithene LPBd



While any base LPBd structure can be chosen for this process, the combination of chain length and C=C structure will significantly affect the properties of the resulting adduct in addition to the number of maleic groups it is realistically possible to graft.

Processing

The highly unsaturated nature of these polymers makes them reactive in both peroxide and sulphur vulcanization systems. In peroxide cures, the Lithenes act as type II coagents, increasing the state of cure and crosslink density by reducing side reactions and forming additional bond points in the cured rubber.

LPBd peroxide cure mechanism:-

•Provides unsaturation which reacts with peroxide radicals or macro radicals

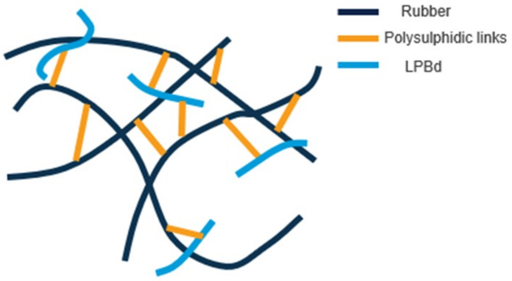
•1,2 vinyl & cyclic vinyl C=C are particularly reactive

•Reduce the effect of competing side reactions for a more effective x-link network

Unlike type I coagents often based on acrylates, LPBd's do not accelerate the rate of cure so provide a good degree of scorch safety.

In sulphur vulcanization, the Lithene again increases cross link density and forms additional linkages to mono, di and polysulphidic types as represented in Figure 3. This provides the compounder with options to modify the physical properties of the vulcanizate in addition to increasing its durability in service.

Figure 3. Lithene LPBd forms additional linkages during vulcanization



LPBd sulphur cure mechanism:-

- Have a high C=C concentration, reactive in sulphur vulcanization
- LPBd's contribute x-link points and different x-link types
- Additional to poly-sulphidic linkages
- Reduces Tg of cured rubber

Regardless of the cure system, addition of an LPBd to a rubber compound will typically reduce the viscosity of the raw compound and assist mixing, potentially reducing mix time. While typical process oils will also perform this function, the LPBd's high degree of unsaturation provides the important advantage that they will chemically cure into the compound during vulcanization, becoming non-extractable. This provides both an environmental benefit as the polymer will not migrate or leach out, as well as ensuring more consistent physical properties through service life.

Experimental

To understand the effect different LPBd structures can have in peroxide & sulphur cured rubbers, two experimental series were designed. Both were based on EPDM rubber.

Peroxide cure

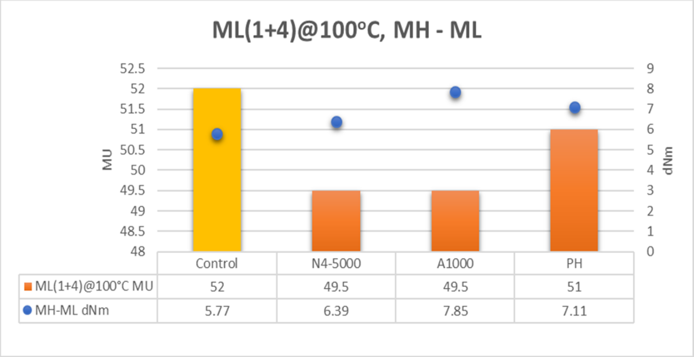
Table 2. Model EPDM peroxide cure recipe

Material	Description	PHR
Vistalon 7500	EPDM Polymer, Mooney 45	100
SRF N-772	Carbon Black	40
SRF N-550	Carbon Black	70
Strukpar 2280	Paraffinic process oil	70
ZnO		5
Stearic acid		1
Perkadox 1440	Peroxide cure agent	6
LPBd	**Type II coagent as silica dry liquid**	**5**

For the peroxide system, a soft, model extrusion recipe was chosen (Table 2), adding the LPBd at 5phr.

Three Lithene LPBd grades, Lithene *ultra* N4-5000, PH and Lithene*ActiV* 1000, as summarised in Table 1, were chosen for comparison. These polymers represent different polymer chain lengths and type of reactive C=C structures. The N4-5000 has a relatively long chain with a higher proportion of in-chain 1,4 C=C, while the other grades have a shorter chain length but higher amounts of C=C in a pendant 1,2 vinyl configuration. Each polymer was pre-mixed to 65% concentration with silica to form a ‘dry liquid’ for ease of mixing with the rubber compound.

Figure 4. ML & MH Lithene LPBd’s peroxide cure

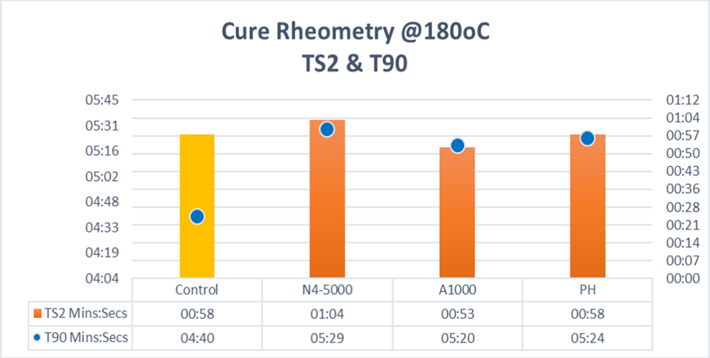


	Control	N4-5000	A1000	PH
■ ML(1+4)@100°C MU	52	49.5	49.5	51
● MH-ML dNm	5.77	6.39	7.85	7.11

The LPBd’s were compounded on a Banbury mixer and evaluated for a range of properties against a control compound containing no coagent.

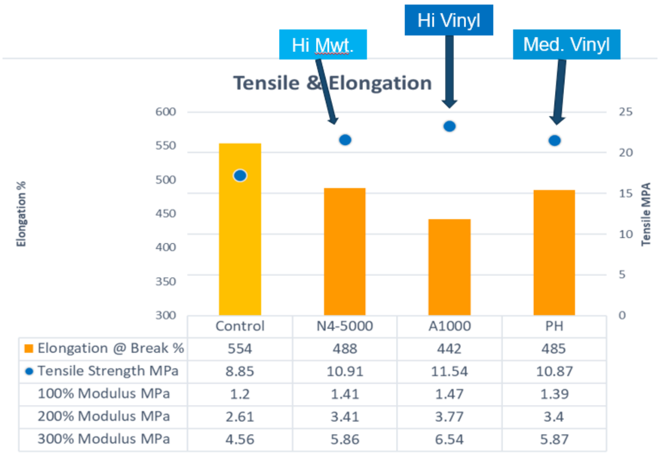
As shown in Figure 4, each LPBd gave lower ML and an increase in delta ML/MH confirming lower mix viscosity and an increase in crosslink density over control. The highest cross link density correlated with the higher 1,2 vinyl content of the Lithene*ActiV* 1000.

Figure 5. Rheometry Lithene LPBd’s peroxide cure



	Control	N4-5000	A1000	PH
■ TS2 Mins:Secs	00:58	01:04	00:53	00:58
● T90 Mins:Secs	04:40	05:29	05:20	05:24

Figure 6. Physical properties Lithene LPBd’s peroxide cure

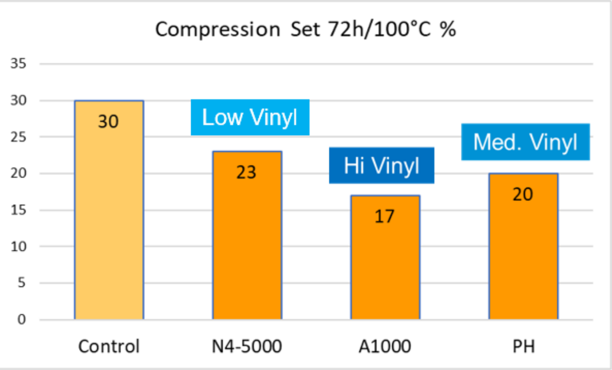


	Control	N4-5000	A1000	PH
■ Elongation @ Break %	554	488	442	485
● Tensile Strength MPa	8.85	10.91	11.54	10.87
100% Modulus MPa	1.2	1.41	1.47	1.39
200% Modulus MPa	2.61	3.41	3.77	3.4
300% Modulus MPa	4.56	5.86	6.54	5.87

Cure rheometry in Figure 5, showed all the LPBd grades to have a similar cure profile and longer T90 values than control, confirming good scorch safety properties.

As can be seen in Figure 6, the physical properties of the cured rubbers also showed a significant contribution from the addition of LPBd with increased tensile strength and modulus. The high 1,2 vinyl content LPBd’s again made the most significant contribution but it was also noted that the longer chain length of the N4-5000 polymer, at least partially compensated for a lower amount of 1,2 vinyl structure.

Figure 7. Compression set Lithene LPBd peroxide



With many peroxide cure rubbers applied to demanding applications such as seals and gaskets in automotive or industrial settings, compression set, oil and solvent resistance can be critical. In Figure 7, all the LPBd’s give a significant reduction in swelling when in contact with xylene and a standard ASTM #3 test oil, as well as lower compression set .

The higher crosslink density afforded by the high 1,2 vinyl LPBd grades was again demonstrated in these tests reflecting the more closely knit structure of the vulcanized rubber incorporating these LPBd's

Sulphur cure

For evaluation in a sulphur cure system, the low 1,2 vinyl content N4-5000 was swapped out with Lithene *ultra* AH, a short chain LPBd with medium 1,2 vinyl content but high proportion of 1,2 cyclic vinyl structure. The three LPBd's chosen, including their typical physical properties, are detailed in Table 3.

Table 3. Lithene LPBd's used in sulphur cure recipe

LPBd	Mwt. Mn (Da)	PDi	1,2 Vinyl %	**Tg**
Lithene *ultra* AH	1300	Broad	45	-31
Lithene *ultra* PH	2600	Broad	45	-70
Lithene*ActiV* 1000	2800	Broad	75	-39

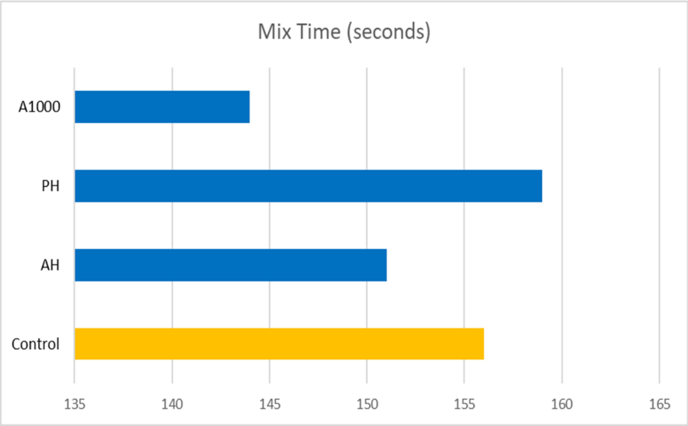
Table 4. Model sulphur cure recipe

Material	**Description**	**PHR**
Royalene 511	EPDM, Mooney 45	100
N762	Carbon Black	50
Paralux 6001	Process Oil	20
ZnO	Zinc Oxide Activator	5
TMQ	Antioxidant	1
MBT	Accelerator	0.1
75% TMTD	Accelerator	1.5
RM-Sulfur	Cure	1.5
Stearic Acid	Activator	1.0
LPBd	Coagent	5.0

Each LPBd was once again added at 5phr and compared against a control in a model EPDM compound recipe (Table 4). Mixing was on a small banbury with mix cycle time determined by reaching a target compound temperature.

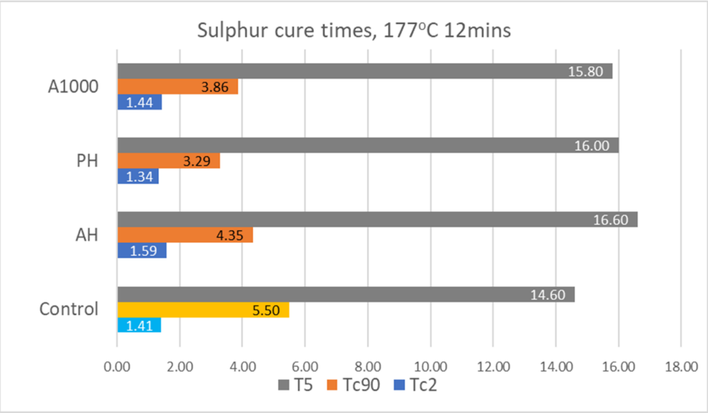
In this compound the LPBd's with the highest total 1,2 vinyl but also high 1,2 cyclic vinyl content, were observed to have reduced the compound mix time appreciably over control. The LPBd's have very low polarity and so generally have good compatibility with EPDM rubbers.

Figure 8. Mix time Lithene LPBd's sulphur cure



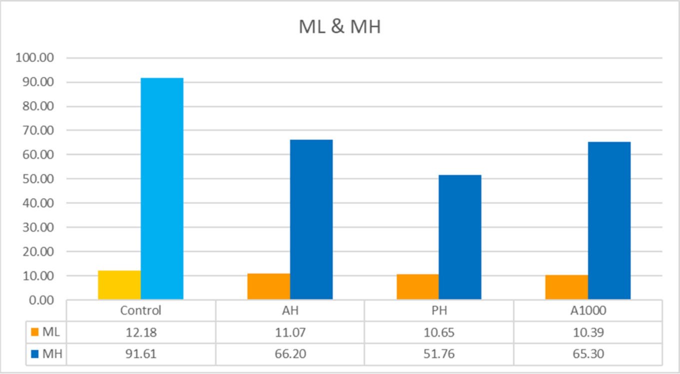
Rheometry again confirmed a low mix viscosity relative to control. In this recipe, initial cure was faster than control but all the LPBd's had a longer T5 Mooney Scorch, suggesting good scorch safety was still maintained.

Figure 9. Rheometry Lithene LPBd's sulphur cure



The different nature of crosslinking and incorporation of LPBd into the rubber matrix in the sulphur cure

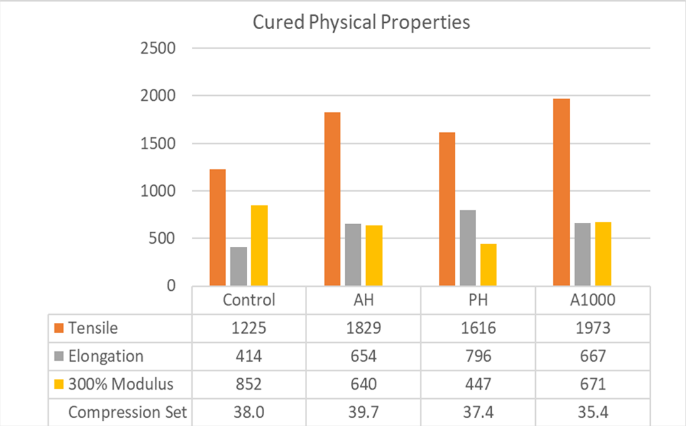
Figure 10. ML & MH Lithene LPBd's sulphur cure



compound, was apparent from the different balance of physical properties measured in comparison to the peroxide cure. In Figure 10, it is seen that while a lower ML value than control was recorded for all LPBd's supporting the mixing and processing benefit, they also achieved a lower MH value than control.

All the LPBd's resulted in a vulcanizate with significantly increased tensile strength and elongation relative to control, with the high 1,2 vinyl content grades AH and ActiV 1000, having the most significant influence on tensile strength (Figure 11). The latter grades also have a small reduction in compression set, but the differences in this compound were relatively small.

Figure 11. Physical properties Lithene LPBd's sulphur cure



	Control	AH	PH	A1000
🟧 Tensile	1225	1829	1616	1973
■ Elongation	414	654	796	667
🟨 300% Modulus	852	640	447	671
Compression Set	38.0	39.7	37.4	35.4

The physical properties resulting from addition of the different LPBd grades are most readily explained by a combination of polymer chain length, position and accessibility of the reactive C=C sites. Given the molecular weight of the LPBd's in this study were between 1300 and 2800 Daltons, the flexibility and strength of the crosslinks formed will be somewhat different to the sulphidic bonds formed in the control compound with no LPBd addition.

While it is beyond the scope of this work to determine the precise mechanism and resulting cross-linked network of these vulcanized compounds, it can reasonably be assumed that the LPBd's have been chemically integrated into the cured rubber network and have a significant effect on the structure.

Rubber to metal adhesion

While the LPBd's discussed so far are reactive in vulcanization, they are apolar in nature. Grafting maleic anhydride functional groups to this backbone significantly increases the polarity of the polymer and offers additional benefits over the non-functional LPBd's. While some C=C bonds are used to attach the maleic group to the polymer backbone, others are still available to react during vulcanization. The MA-LPBd's are therefore still non-extractable but their higher polarity assists with both filler dispersion during compound mixing and improving the bond between rubber and metal or fabrics in reinforced articles.

- ➢ Maleic anhydride increases polarity
- ➢ Improved filler dispersion
- ➢ Backbone C=C Vulcanizes with rubber
- ➢ Increased adhesion to metals & fabrics
- ➢ Longer chain = higher functionality

One excellent demonstration of both non functional and maleic anhydride functional LPBd's properties, is seen in the automotive industry. LPBd's are both adhesive and have excellent sound damping properties, so are used in a variety of automotive adhesives, sealants and damping compounds, in either peroxide or sulphur vulcanized systems.

MA-LPBd's contribute to these properties but are used mainly as adhesion promoters. These sealants are

applied in the automotive bodyshop, directly to metal body shell surfaces still coated with anti-corrosive oil.

As pure hydrocarbons, the LPBd's are highly compatible with such oils so can be applied without the need for firstly degreasing the surface to remove the oil. Vulcanization takes place in-line using the high temperature e-coat primer curing ovens, prior to the final colour coat and lacquer application in the paint shop.

In the model sulphur cure recipe shown in Table 5, an MA-LPBd is combined with a non-functional LPBd as the main binder. The sealant is applied to two oiled, steel test panels and cured at 170°C for 30 minutes to form a bond between the two strips.

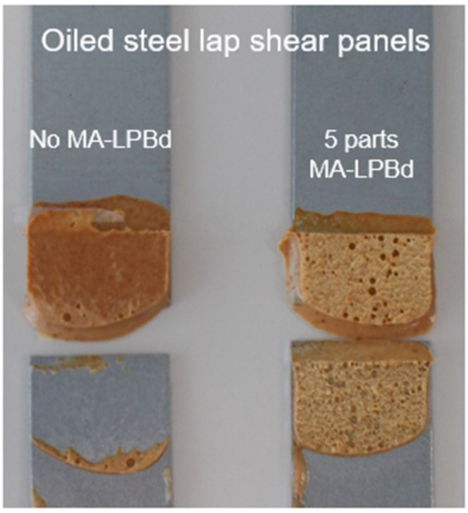
Table 5. Model automotive sealant recipe, sulphur cure

Material	Function	Addn. %
LPBD	Main Binder	**30**
MA-LPBD	**Adhesion promotor**	**5**
Sulphur	Vulcanization reagent	4.0 - 6.9
MBTS	Accelerator	3
ZnO	Cure activator	3
CaO	Desiccant	2
ZBeD	Secondary accelerator	0.18
Antioxidant		0.2
Silica	Filler	2
Carbonate	Filler	47.73

The strips were then pulled apart on a tensile tester and both the bond strength and failure mechanism determined. It is typically desirable for a cohesive failure to occur within the adhesive itself rather than between the adhesive and metal.

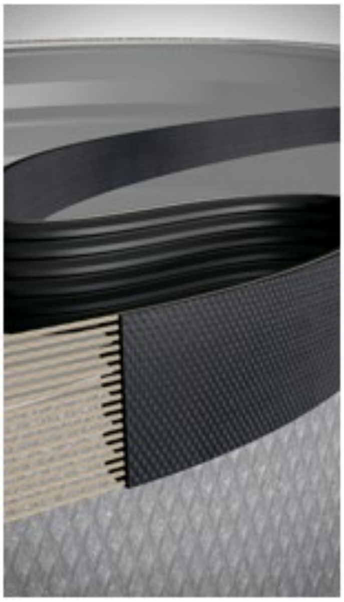
As can be seen clearly from Figure 12, the adhesive containing no MA-LPBd loses adhesion completely with one metal surface while the other containing 5 parts MA-LPBd retains adhesion to both oiled steel strips. This has important benefits for automotive OEM's as any failure of such an adhesive bond would result in unprotected metal being exposed providing a route for the onset of corrosion.

Figure 12. MA-LPBd adhesion promoter, bonding to oiled steel after lap shear.



In reinforced rubbers, while corrosion may not be the primary concern, effective rubber to metal or rubber to fabric bonding is always required. The MA-LPBd's have good compatibility with the rubber matrix and will readily vulcanize, while the maleic anhydride functionality provides good substrate bonding.

While specific adhesion data is not presented here, MA functional Lithene grades such as AL-15MA and N4-5000-15MA find commercial application in assisting reinforcement adhesion in automotive drive belts, hoses and conveyor belts.



Summary

This article has sought to describe the physical nature and benefits of pure liquid polybutadienes and their maleic anhydride derivatives, in a variety of rubber compounding applications. With a wide choice of polymer chain lengths and reactive C=C structures, Lithene liquid polybutadienes offer the rubber formulator improved performance from compound mixing through to the end product. The high degree of unsaturation enables the LPBd's to co-cure with the rubber, contributing additional bond points, becoming chemically bound and non-extractable from the rubber matrix.

Lithene™ Liquid Polybutadiene Key Properties

- Non hazardous 100% liquid polymers
- Various structures & chain lengths → optimized performance
- Reactive in peroxide or sulphur cures
- Maleic anhydride functional → rubber to metal bonding

These non hazardous polymers can have a positive impact on mixing operations by reducing mix viscosity and potentially cycle time by enabling more efficient mixing in either their pure liquid or dispersed silica dry liquid form.

Good scorch safety in both sulphur and peroxide cures, was also demonstrated and careful choice of LPBd grade was shown to provide a range of physical performance enhancements including tensile strength and compression set.

Mixer

- **Non-polar liquid polymers**
- **Better compound mixing**
- **Shorter mix time**

Moulding & cure

- **Lower mix viscosity**
- **Good scorch safety**

Product

- **Improved physicals**
- **Better compression set**
- **Non leaching**

Maleic anhydride functional LPBd's also co-cure with the rubber and offer the potential of increased adhesion to metals or fabrics, acting as a bridge between the rubber matrix and reinforcement surface.

While this article has presented examples in EPDM based compounds both peroxide and sulphur cured, other vulcanized rubber types including BR, SBR and HNBR are also relevant to consider for modification by liquid polybutadienes.

Lithene™ *Liquid Polybutadienes are commercially available from Synthomer (UK) Ltd.*
Rubber study practical work carried out by TARRC, Hertford, UK (peroxide study), ACE Consulting, Ravenna OH, USA (sulphur study), Synthomer (UK) Ltd. (Automotive adhesion study)